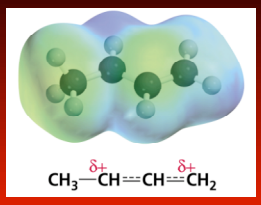


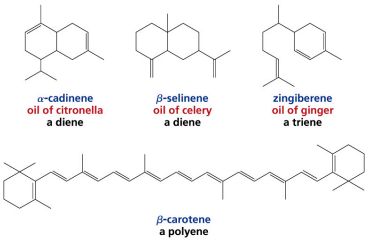
Dienes

Chapter 8

Adapted from Turro & Breslow, Columbia University and Irene Lee, Case Western Reserve University

Unsaturated hydrocarbons containing:

two double bonds: diene
three double bonds: triene
four double bonds: tetraene
many double bonds: polyene



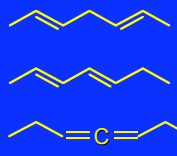
α-cadinene
oil of citronella
a diene

β-selinene
oil of celery
a diene

zingiberene
oil of ginger
a triene

β-carotene
a polyene

Classification of Dienes

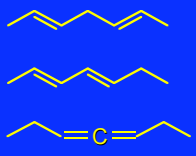


isolated diene

conjugated diene

cumulated diene

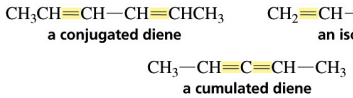
Nomenclature

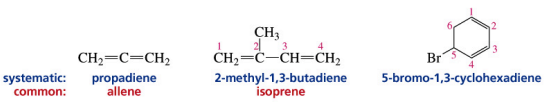


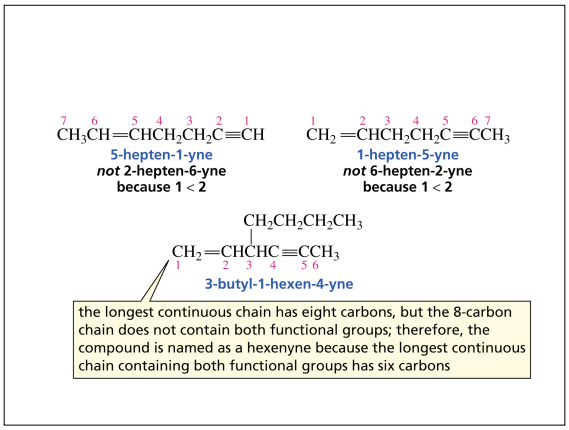
(2*E*,5*E*)-2,5-heptadiene

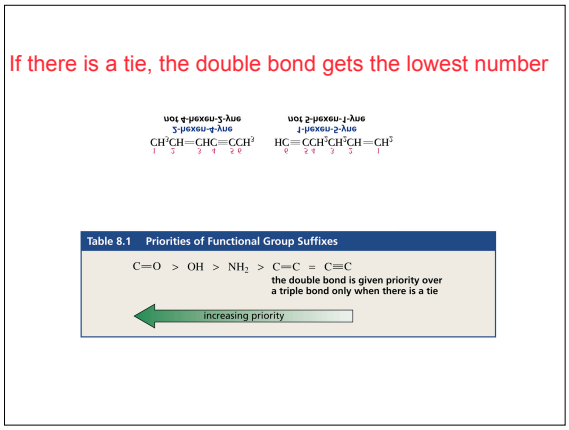
(2*E*,4*E*)-2,4-heptadiene

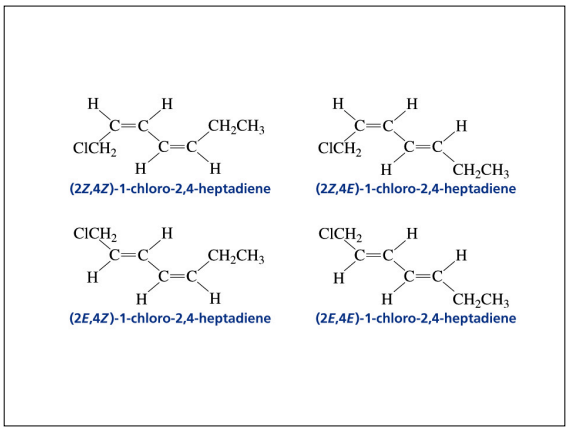
3,4-heptadiene

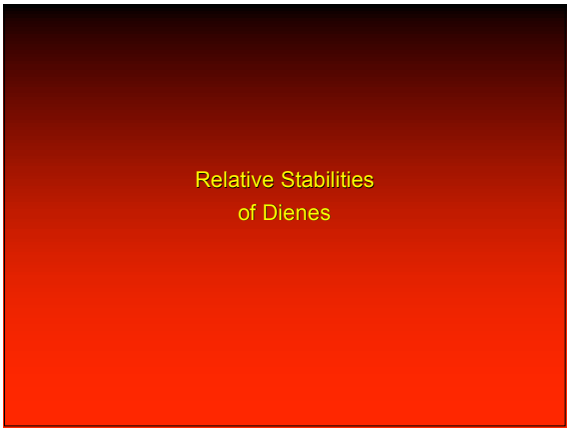


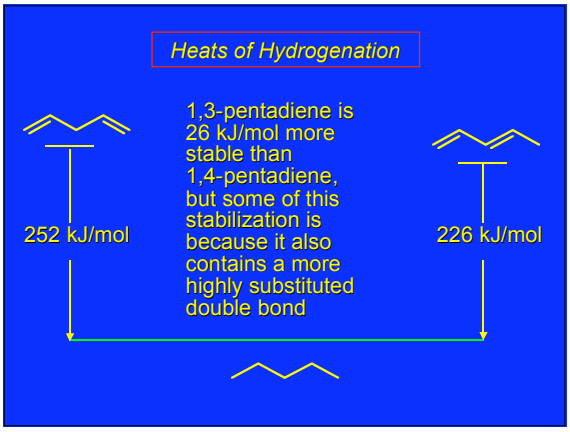


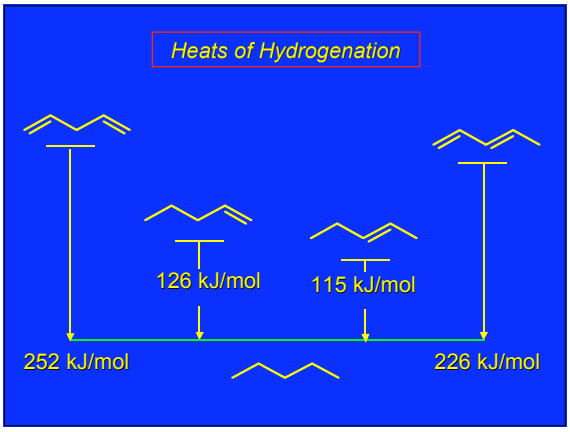

7 6 5 4 3 2 1
CH3CH=CHCH2CH2C≡CH
5-hepten-1-yne
not 2-hepten-6-yne
because 1 < 2
1 2 3 4 5 6 7
CH2=CHCH2CH2C≡CCH3
1-hepten-5-yne
not 6-hepten-2-yne
because 1 < 2
CH2CH2CH2CH3
CH2=CHCHC≡CCH3
1 2 3 4 5 6
3-butyl-1-hexen-4-yne
the longest continuous chain has eight carbons, but the 8-carbon chain does not contain both functional groups; therefore, the compound is named as a hexenyne because the longest continuous chain containing both functional groups has six carbons


If there is a tie, the double bond gets the lowest number
Table 8.1 Priorities of Functional Group Suffixes
C=O > OH > NH2 > C=C = C≡C
the double bond is given priority over a triple bond only when there is a tie
increasing priority

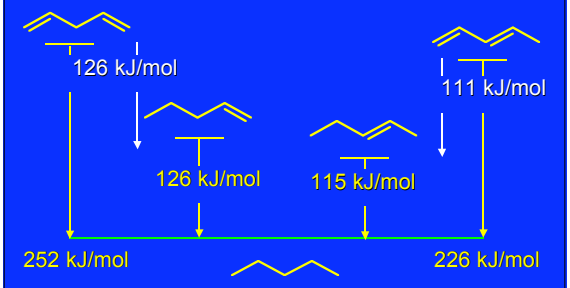

(2Z,4Z)-1-chloro-2,4-heptadiene
(2Z,4E)-1-chloro-2,4-heptadiene
(2E,4Z)-1-chloro-2,4-heptadiene
(2E,4E)-1-chloro-2,4-heptadiene


Relative Stabilities
of Dienes

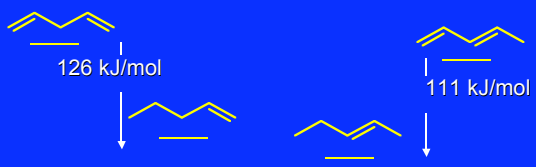

Heats of Hydrogenation
252 kJ/mol
1,3-pentadiene is 26 kJ/mol more stable than 1,4-pentadiene, but some of this stabilization is because it also contains a more highly substituted double bond
226 kJ/mol


Heats of Hydrogenation
126 kJ/mol
115 kJ/mol
252 kJ/mol
226 kJ/mol

Heats of Hydrogenation

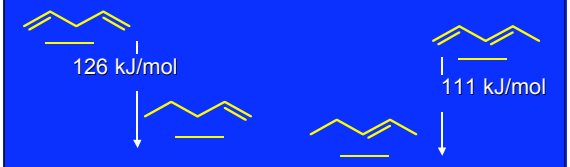


Heats of Hydrogenation



when terminal double bond is conjugated with other double bond, its heat of hydrogenation is 15 kJ/mol less than when isolated

Heats of Hydrogenation



this extra 15 kJ/mol is known by several terms
- stabilization energy
- delocalization energy
- resonance energy

Heats of Hydrogenation

Cumulated double bonds have relatively high heats of hydrogenation

$H_2C{=}C{=}CH_2 + 2H_2 \longrightarrow CH_3CH_2CH_3$

$\Delta H° = -295$ kJ

$H_2C{=}CH_2CH_3 + H_2 \longrightarrow CH_3CH_2CH_3$

$\Delta H° = -125$ kJ

relative stabilities of dienes

conjugated diene > isolated diene > cumulated diene

increasing stability

$CH_3CH{=}C{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -70.5$ kcal/mol (−295 kJ/mol)
2,3-pentadiene

$CH_2{=}CHCH_2CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -60.2$ kcal/mol (−252 kJ/mol)
1,4-pentadiene

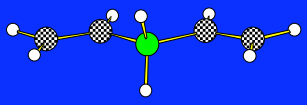
$CH_2{=}CHCH{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ $\Delta H° = -54.1$ kcal/mol (−226 kJ/mol)
1,3-pentadiene

Table 8.2 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation

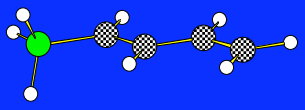
Compound	Hybridization	Bond length (Å)
$H_3C{-}CH_3$	sp^3–sp^3	1.54
$H_3C{-}\overset{H}{\overset{\vert}{C}}{=}CH_2$	sp^3–sp^2	1.50
$H_2C{=}\overset{H}{\overset{\vert}{C}}{-}\overset{H}{\overset{\vert}{C}}{=}CH_2$	sp^2–sp^2	1.47
$H_3C{-}C{\equiv}CH$	sp^3–sp	1.46
$H_2C{=}\overset{H}{\overset{\vert}{C}}{-}C{\equiv}CH$	sp^2–sp	1.43
$HC{\equiv}C{-}C{\equiv}CH$	sp–sp	1.37

Bonding
in Conjugated Dienes

Isolated diene



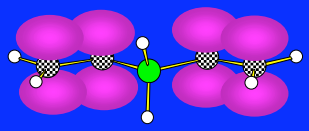
1,4-pentadiene



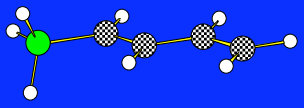
1,3-pentadiene

Conjugated diene

Isolated diene



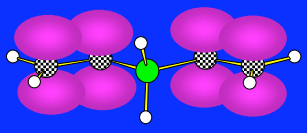
π bonds are independent of each other



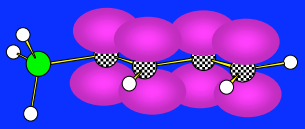
1,3-pentadiene

Conjugated diene

Isolated diene



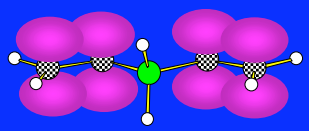
π bonds are independent of each other



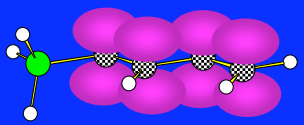
p orbitals overlap to give extended π bond encompassing four carbons

Conjugated diene

Isolated diene



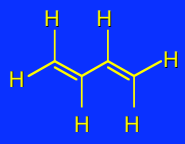
less electron delocalization; less stable



more electron delocalization; more stable

Conjugated diene

Conformations of Dienes



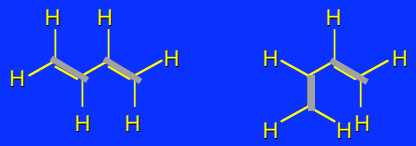
s-trans

s-cis

s prefix designates conformation around single bond

s prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates configuration and is upper case)

Conformations of Dienes

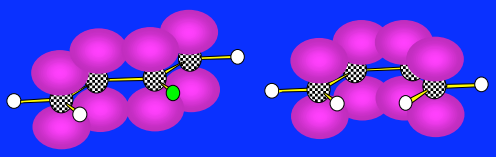


s-trans *s*-cis

s prefix designates conformation around single bond

s prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates configuration and is upper case)

Conformations of Dienes

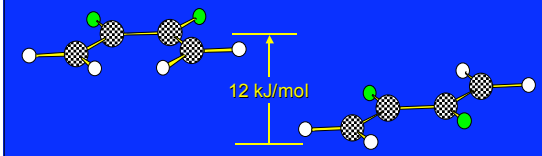


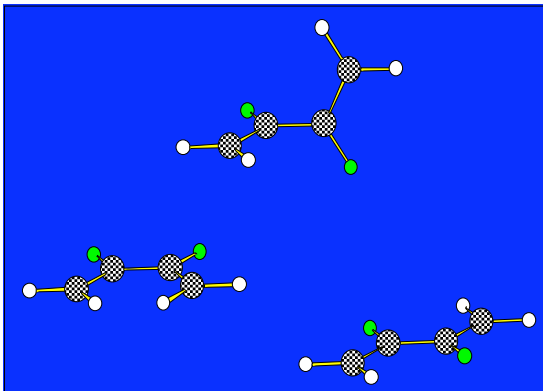
s-trans *s*-cis

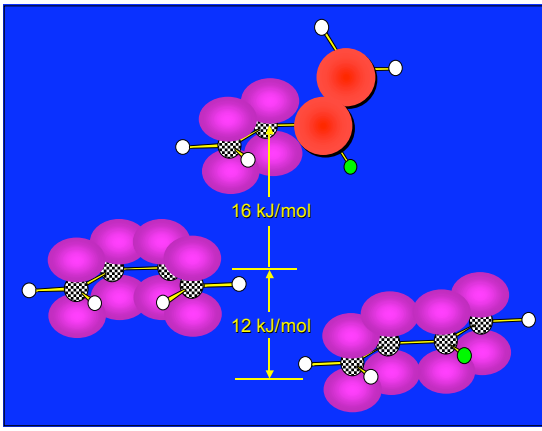
Both conformations allow electron delocalization via overlap of *p* orbitals to give extended π system

s-trans is more stable than s-cis

Interconversion of conformations requires two π bonds to be at right angles to each other and prevents conjugation

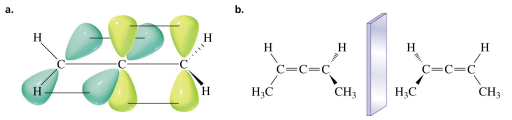




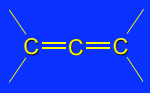


Bonding in Allenes

A cumulated diene is less stable than an isolated diene

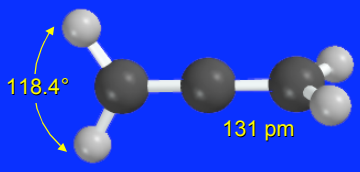


Cumulated Dienes



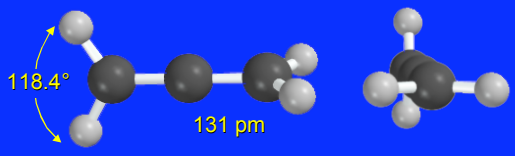
cumulated dienes are less stable than isolated and conjugated dienes

Structure of Allene



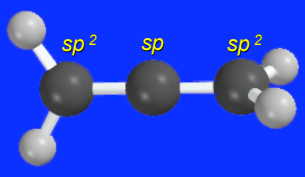
linear arrangement of carbons
nonplanar geometry

Structure of Allene

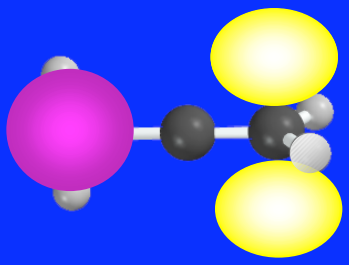


linear arrangement of carbons
nonplanar geometry

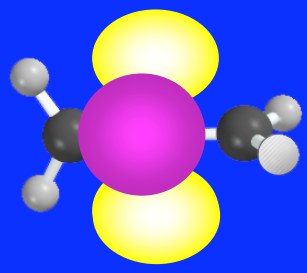
Bonding in Allene



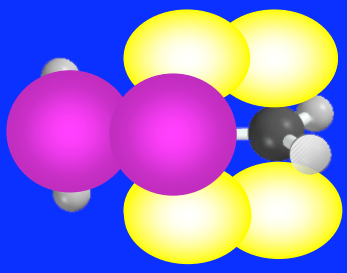
Bonding in Allene



Bonding in Allene

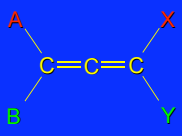


Bonding in Allene



Chiral Allenes

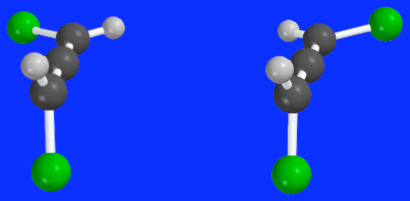
Allenes of the type shown are chiral



A ≠ B; X ≠ Y

Have a stereogenic axis

Stereogenic Axis



analogous to difference between:

a screw with a right-hand thread and one with a left-hand thread

a right-handed helix and a left-handed helix